Radiochim. Acta **101**, 133–138 (2013) / **DOI** 10.1524/ract.2013.2022


# Thermodynamics of Np(IV) complexes with gluconic acid under alkaline conditions: sorption studies

By H. Rojo[1,*], J. Tits[2], X. Gaona[3], M. Garcia-Gutiérrez[1], T. Missana[1] and E. Wieland[2]

[1] Sorption, Migration and Colloids Laboratory, CIEMAT, Madrid, Spain
[2] Laboratory for Waste Management, Paul Scherrer Institut, Villigen PSI, Switzerland
[3] Institut für Nukleare Entsorgung, Karlsruhe Institute of Technology, Karlsruhe, Germany

(Received April 17, 2012; accepted in revised form August 28, 2012)
(Published online February 25, 2013)

*Neptunium(IV) / Gluconate / Complexation / Sorption / Thermodynamic description*

**Summary.** The complexation of Np(IV) with gluconic acid (GLU) under alkaline conditions was investigated in the absence of Ca by carrying out a series of sorption experiments. The decrease of Np(IV) sorption on the sorbing material at increasing concentrations of GLU was interpreted as the formation of Np(IV)-GLU aqueous complexes. The modelling of experimental data according to the Schubert method [1] confirmed the formation of a complex with a Np : GLU ratio 1 : 1. The stoichiometry of the complex $Np(OH)_4GLU^-$ was proposed based on the experimental observation that no proton exchange occurred during the course of the complexation reaction and that $Np(OH)_4(aq)$ was the predominant hydrolysis product in the absence of GLU. A $\log {}^*\beta^0_{1,4,1} = -2.92 \pm 0.30$ for the formation reaction $Np^{4+} + 4H_2O + GLU^- \Leftrightarrow Np(OH)_4GLU^- + 4H^+$ was calculated based on the conditional stability constants determined from sorption experiments and using the Np(IV) thermodynamic data selected in the NEA reviews [2].

Linear free energy relationships (LFER) confirmed that the stoichiometry and stability of the Np(IV)-GLU complex characterized in this work are consistent with data available for Th(IV)-, U(IV)- and Pu(IV)-GLU complexes.

## 1. Introduction

The use of cement and concrete is envisaged in deep geological repositories for low and intermediate level wastes (L/ILW) in Switzerland. Retention by cementitious materials is one of the fundamental processes expected to delay the migration of radionuclides from the repository near-field into the host rock.

Understanding the behaviour of neptunium is important for performance assessment (PA) because of its redox-sensitive character and very long half-life ($t_{1/2} = 2.14 \times 10^6$ y). Under the reducing alkaline conditions expected to prevail in a cementitious near-field, Np will be found predominantly in the tetravalent state, according to thermodynamic data available for this actinide [2]. Under the same boundary conditions, polyhydroxocarboxylic acids, which are generated during the course of cellulose degradation (*e.g.* isosaccharinic acid, ISA) or used as cement admixture (*e.g.* gluconic acid, GLU), are expected to be present. GLU concentrations in cement could be as high as $10^{-2}$ M on the assumption that GLU is entirely released into the pore water, although sorption by cement surfaces may reduce this concentration to values below $10^{-7}$ M [3].

The formation of very stable complexes of An(III) and An(IV) with ISA and GLU has been reported in the literature [4–7]. The stability of An(IV)-GLU complexes seems to be further increased in the presence of Ca, where ternary Ca-An(IV)-GLU complexes have been described for Th(IV). Despite the relevance of Np(IV) and GLU in the context of cement-based repositories, no experimental studies are available in the literature dealing with the formation of Np(IV)-GLU complexes.

The present study aimed at investigating the complexation of Np(IV) with GLU under alkaline conditions and in absence of Ca by conducting a series of sorption experiments under reducing conditions at different pH and GLU concentrations. Neptunium was kept in its tetravalent state by the addition of a reducing agent (Na-dithionite, $Na_2S_2O_4$). The Schubert method [*e.g.* 1, 4, 6, 8] was applied to determine the stoichiometry and the stability constants of the Np(IV)-GLU complexes. The resulting thermodynamic data were compared with data available for other An(IV)-GLU complexes.

## 2. Materials and methods

### 2.1 Materials

All experiments were performed at $23 \pm 2$ °C in a glovebox under $N_2$ atmosphere ($O_2$, $CO_2 < 5$ ppm). Merck "pro analysis" chemicals were used. Solutions were prepared using deionized, decarbonated water (Milli-Q water) generated by a Milli-Q Gradient A10 System (Millipore, Bedford, USA). Samples were prepared in 40 mL polyallomere centrifuge tubes (Beckmann Instruments Inc.), previously washed with Deconex (Borer Chemie AG, Zuchwil, Switzerland), left overnight in a solution of 0.1 M HCl, and thoroughly rinsed with Milli-Q water. A cation exchange resin Bio-Rad 50W-X2 (Bio-Rad Laboratories, Hercules, USA) was used as sorbent material. Before use, this resin was washed and

*Author for correspondence (E-mail: henar.rojo@psi.ch).

conditioned following a procedure described elsewhere [4]. Gluconic acid was available as a Na salt (Merck AG, Dietikon, Switzerland).

### 2.2 Radiotracers

A short-lived ($t_{1/2} = 2.35$ d) $^{239}$Np tracer solution was used in all experiments. This isotope was obtained by extraction from a stock solution containing $3.40 \times 10^{-7}$ M of $^{243}$Am (Eckert & Ziegler Isotope Products, USA) following a procedure described elsewhere [9]. Briefly, $^{239}$Np in secular equilibrium with $^{243}$Am, was stabilized as Np(V) in the feed solution with hydrochloric acid, extracted into a triisooctylamine/xylene phase and then back-extracted with Milli-Q water. This milking procedure could be repeated every two weeks, as a result of the different half-lives of $^{243}$Am and $^{239}$Np (7370 y and 2.35 d, respectively). The radiochemical purity of the neptunium tracer solution was checked in each experiment by gamma spectroscopy, indicating in all cases a content of $^{243}$Am below 5%. The starting activity of the $^{239}$Np tracer was $\sim 37$ MBq/20 mL.

$^{228}$Th radiotracer ($\alpha$-emitter, $t_{1/2} = 1.91$ y) was purchased from Eckert & Ziegler Isotope Products, USA.

### 2.3 Experimental set-up

Appropriate amounts of conditioned cation exchange resin were mixed with either a 0.3 M NaOH solution or a 0.3 M $NaClO_4$ solution. The ionic strength was fixed at 0.3 M either with $NaClO_4$ (experiments at pH = 11) or NaOH (experiments at pH = 13.3). Reducing conditions were ensured by the addition of 0.1 M $Na_2S_2O_4$ aiming at a final concentration of $5 \times 10^{-3}$ M.

For sorption kinetic tests, 4 mL aliquots of ion exchange resin were withdrawn from a vigorously stirred resin suspension with a solid-to-liquid ratio (S : L) of $10^{-2}$ kg L$^{-1}$ and transferred into polyallomere centrifuge tubes together with 2 mL 0.1 M $Na_2S_2O_4$ solution. The tubes were filled up to 40 mL with 34 mL 0.3 M NaOH solution and spiked with 0.6 mL $^{239}$Np stock solution. The final S : L ratio was $10^{-3}$ kg L$^{-1}$.

To test the effect of $Na_2S_2O_4$ addition on the sorption of the tetravalent actinides, kinetic tests similar to those described above, were carried out with Th(IV) at pH 13.3 in the absence and presence of $5 \times 10^{-3}$ M $Na_2S_2O_4$. 2 mL 0.1 M $Na_2S_2O_4$ solution were added to aliquots of the suspensions and spiked with 0.05 mL of a 1.08 MBq $^{228}$Th tracer solution.

The influence of the S : L ratio was tested by mixing varying amounts of resin with 2 mL 0.1 M $Na_2S_2O_4$ and 38 mL 0.3 M NaOH into polyallomere centrifuge tubes. The suspensions were spiked with 0.6 mL $^{239}$Np stock solution. The total volume was 40 mL.

Sorption experiments in the presence of increasing GLU concentrations were set up by mixing 4 mL of a vigorously stirred resin suspension (final S : L = $10^{-3}$ kg L$^{-1}$ or $10^{-2}$ kg L$^{-1}$) with appropriate amounts of 0.3 M NaOH or $10^{-3}$ M NaOH, respectively, 3 M $NaClO_4$ to fix the ionic strength in the samples with pH 11 and GLU solutions ($2 \times 10^{-5}$ M, $2 \times 10^{-3}$ M, $2 \times 10^{-1}$ M) together with 0.6 mL of $^{239}$Np tracer solution.

In all the experiments the pH was adjusted with 1 M NaOH. The tubes were put on an end-over-end shaker for equilibration. Samples were collected after regular time intervals in the case of the sorption kinetic tests and after 2 days for the other experiments. Tables 1 and 2 summarize the experimental conditions considered in the sorption experiments of this study.

After the considered equilibration time, the redox potential and the pH of the samples were determined with a Metrohm combined glass electrode and a Metrohm combined redox electrode (with Ag/AgCl reference), respectively. Phase separation was achieved by centrifuging the samples for 1 h at 90 000 g (max). The $^{228}$Th or $^{239}$Np activities in the supernatant solutions were analysed by liquid scintillation counting (LSC) using a Tri-Carb™ 2750A liquid scintillation analyzer equipped with an alpha-beta discrimination option (Perkin Elmer, USA). Prior to LSC analysis, the supernatant samples were mixed with scintillation cocktail (Ultima Gold XR, Perkin Elmer, USA, in the case of alkaline $^{239}$Np samples and Ultima Gold AB, Perkin Elmer, USA, in the case of acid $^{239}$Np and $^{228}$Th samples at ratios of 1 : 3 and 3 : 17, respectively). $^{228}$Th samples were stored for one month before LSC measurements in order to allow secular equilibrium with its daughters to be re-established.

In the case of cations such as Np(IV) and Th(IV), strong sorption is known to take place on the walls of the centrifuge tubes as well. This wall sorption has been previously shown to depend on the complexation with organic ligands such as GLU [4]. Therefore, in order to evaluate the sorption of $^{239}$Np on the tubes walls, the centrifuge tubes were emptied after sampling, rapidly rinsed with 10 mL of a solution identical to the one used in the preceding sorption test but without $^{239}$Np tracer and then filled with 20 mL 1 M HCl solution to allow desorption of the radionuclide from the walls. Duplicate samples were taken from these solutions after one day of equilibration and analysed for their $^{239}$Np activities using LSC as described above.

The sorption of Np(IV) and Th(IV) was quantified by measuring the partitioning of the radionuclides between the

**Table 1.** Experimental conditions in test experiments evaluating kinetics, effect of $Na_2S_2O_4$ and effect of S : L.

| Test experiment | Radionuclide | $[An(IV)]_0$ (M) | pH | S : L ratio (kg L$^{-1}$) | Equil. time (d) |
|---|---|---|---|---|---|
| Kinetics/effect of $Na_2S_2O_4$ | Th(IV) | $3.7 \times 10^{-9}$ | 13.3 | $1 \times 10^{-3}$ | 1–11 |
| | Np(IV) | $1.5 \times 10^{-11}$ | 13.3 | $1 \times 10^{-3}$ | 1–9 |
| Effect of S : L | Np(IV) | $6.4 \times 10^{-12}$ | 13.3 | $2 \times 10^{-3}$–$2 \times 10^{-2}$ | 2 |

**Table 2.** Experimental conditions of Np(IV) sorption experiments in the presence of GLU.

| pH | $E_h$ (mV) | $[Np(IV)]_0$ (M) | S : L ratio (kg L$^{-1}$) | [GLU] (mol L$^{-1}$) | Equil. time (d) |
|---|---|---|---|---|---|
| 13.3 | $-1011 \pm 50$ | $1.9 \times 10^{-11}$ | $1 \times 10^{-3}$ | $10^{-7}$–$10^{-3}$ | 2 |
| | $-965 \pm 50$ | $5.3 \times 10^{-12}$ | $1 \times 10^{-2}$ | $10^{-7}$–$10^{-3}$ | 2 |
| 11.0 | $-813 \pm 50$ | $5.4 \times 10^{-12}$ | $1 \times 10^{-3}$ | $10^{-7}$–$10^{-3}$ | 2 |

solid and the liquid phase, which can be described in terms of a distribution coefficient $R_d$ (L kg$^{-1}$):

$$R_d = \left(\frac{A_{solid}}{A_{eq}}\right) \cdot \left(\frac{V}{W}\right) \quad (L\,kg^{-1}) \tag{1}$$

with $A_{solid}$ = activity of the radionuclide sorbed on the solid (cpm L$^{-1}$), $A_{eq}$ = activity of the radionuclide in the equilibrium solution (cpm L$^{-1}$), $V$ = volume of the suspension (L), $W$ = mass of solid (kg).

In the present work, sorption on the walls was used as an additional source of data for the determination of the formation constants and stoichiometries of the Np(IV) – GLU complexes. $R_d$ values for wall sorption were calculated by assuming an arbitrary S : L ratio of 0.1 kg L$^{-1}$. Eq. (1) was accordingly modified to calculate $R_d$ values in the case of wall sorption:

$$R_{d\,walls} = \left(\frac{A_{wall}}{A_{eq}}\right) \cdot 10 \quad (L\,kg^{-1}) \tag{2}$$

### 2.4 Determination of the stoichiometry and stability constants of Np(IV)-GLU complexes: theory

The stoichiometry and the stability constants of the Np(IV)-GLU complexes forming in the conditions of the experiment were determined in accordance with the Schubert method [1, 4, 6, 8]. The method is based on the analysis of the effect of increasing ligand concentration on the sorption of a metal/radionuclide on a solid phase. The decrease in sorption caused by the formation of a complex in the aqueous phase can be directly related to the stoichiometry and stability constant of the complex. Application of the Schubert method requires that: (1) the chemical system is at equilibrium, (2) the sorption of the metal/radionuclide on the solid phase is linear, (3) the sorption reaction is reversible and, (4) neither the free ligand nor the complex sorb on the solid phase.

In analogy with ISA [4, 10], and consistently with other tetravalent actinides such as Th(IV) [7], Np(IV)-GLU complexation in the absence of Ca can be described by the general reaction:

$$Np^{4+} + nGLU^- + mH_2O \Leftrightarrow Np(OH)_m(GLU)_n^{\,4-m-n} + mH^+ \tag{3}$$

where GLU$^-$ represents the GLU ligand with one deprotonated carboxyl group. Note that several authors have suggested the deprotonation of some of the alcohol groups within the process of complex formation (see [7] and references therein). Although likely, this possibility does not influence the overall stoichiometry of the reaction if protonation/deprotonation processes are considered within the hydrolysis of An(IV). In this work, H$^+$ release/uptake in the complexation reaction was assumed to uniquely correspond to the hydrolysis of Np(IV). The complexation constant, ${}^*\beta^0_{1,m,n}$ can be defined in accordance with reaction Eq. (3):

$${}^*\beta^0_{1,m,n} = \frac{\left[Np(OH)_m(GLU)_n^{\,4-m-n}\right] \cdot [H^+]^m}{[Np^{4+}] \cdot [GLU^-]^n} \cdot \frac{\gamma_{Np(OH)_m(GLU)_n^{\,4-m-n}} \cdot \gamma_{H^+}^m}{\gamma_{Np^{4+}} \cdot \gamma_{GLU^-}^n} \tag{4}$$

where brackets denote molar concentrations of the species and $\gamma_i$ are the corresponding activity coefficients.

Considering the formation of a Np(IV)-GLU complex, the $R_d$ value can be written as follows:

$$\log R_d = \log R_d^0 - \log\left(1 + \frac{{}^*\beta_{1,m,n}}{A \cdot [H^+]^m} \cdot [GLU^-]_{free}^n\right) \tag{5}$$

where $R_d^0$ is the distribution coefficient determined in the absence of GLU; [GLU$^-$] and [H$^+$] are the free concentrations of GLU and protons in solution, respectively; ${}^*\beta_{1,m,n}$ is the conditional stability constant for reaction Eq. (3) at $I$ = 0.3 M; $A$ is the side reaction coefficient accounting for the hydrolysis of Np(IV); $n$ is the number of GLU in the complex and $m$ is the number of protons involved in the complexation reaction. Due to the absence of Ca in the system and the very low Np(IV) concentration, $[GLU^-]_{free}$ could be considered equal to $[GLU^-]_{tot}$ in the fit of the experimental data.

Speciation calculations conducted using the NEA thermodynamic database [2] and the Medusa speciation code [11] indicated that Np(OH)$_4$(aq) is the predominant aqueous species present under the pH and $E_h$ conditions of this study in absence of GLU. Hence, the side reaction coefficient ($A$) can be approximated by:

$$A = 1 + \frac{{}^*\beta_{1,4}}{[H^+]^4} \tag{6}$$

with ${}^*\beta_{1,4}$ being the conditional stability constant at $I$ = 0.3 M for the formation of Np(OH)$_4$(aq), as derived from the application of the Davies equation to $\log {}^*\beta^0_{1,4} = -8.3 \pm 1.1$ for the equilibrium reaction $Np^{4+} + 4H_2O \Leftrightarrow Np(OH)_4(aq) + 4H^+$ [2]. In this study, $A$ is constant as a result of constant pH and $I$.

Eq. (5) can be further re-arranged to obtain a linear relationship with respect to log [GLU$^-$]:

$$\log\left(\frac{R_d^0}{R_d} - 1\right) = \log\left(\frac{{}^*\beta'_{1,m,n}}{A}\right) + n \cdot \log\left[GLU^-\right] \tag{7}$$

where

$${}^*\beta'_{1,m,n} = {}^*\beta_{1,m,n} / \left[H^+\right]^m$$

In a first step, the number of GLU involved in the complexation reaction ($n$) was determined by separately applying Eq. (5) to experiments at different pH (13.3 and 11), and therefore considering the term ${}^*\beta_{1,m,n}/[H^+]^m$ to be a constant. Hence, Eq. (5) was fitted to the available experimental data, and $n$ was determined for each case. In a second step, $\log {}^*\beta'_{1,m,n}$ was plotted against pH, and $m$ was determined from the slope of the corresponding linear fit. Finally, an unweighted average of $\log {}^*\beta_{1,m,n}$ was calculated and corrected to $I$ = 0 using the Davies equation [12] in order to determine ${}^*\beta^0_{1,m,n}$.

## 3. Results and discussion

### 3.1 Effect of kinetics, $Na_2S_2O_4$ and S : L

Prior to the sorption experiments in the presence of GLU, a series of test experiments were carried out with the aim of assessing whether the conditions under which the Schu-

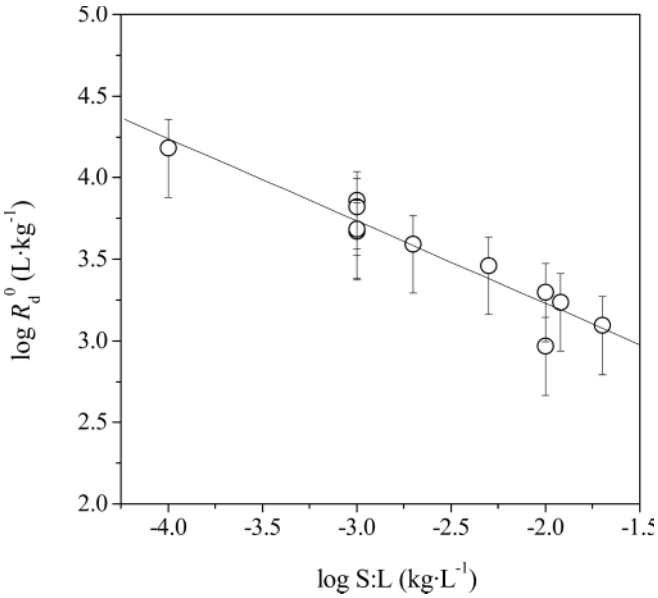


**Fig. 1.** Effect of S : L ratio on the sorption of Np(IV) on Bio-Rad resin in the absence of GLU in 0.3 M NaOH (pH = 13.3) ($R_d^0$). Equilibration time: 2 days.

bert method can be applied (see Sect. 2.4) were met and also to exclude possible artefacts originating from the presence of $Na_2S_2O_4$. These test experiments included the effect of the reaction time (kinetics), the presence of $Na_2S_2O_4$ and the S : L ratio on the sorption of Np(IV). In view of the extremely low Np concentration in the experiments, it was considered that its sorption behaviour is linear. Furthermore, it is expected that the negative charge existing at the surface of the cation exchange resin prevents the $GLU^-$ anions and the metal-ligand complexes from sorbing on the solid.

Kinetic experiments conducted with Th(IV) and Np(IV) in the absence of GLU indicated that the equilibrium is reached after approximately 2 days (data not shown). Accordingly, this equilibration time was considered in the following experiments.

Very similar $R_d^0$ values were obtained for Th(IV) sorption on the Bio-Rad 50W-X2 resin in the absence and in the presence of $5 \times 10^{-3}$ M $Na_2S_2O_4$ (log $R_d^0 \sim 4$–4.5 L kg$^{-1}$). This observation indicates that neither $Na_2S_2O_4$ nor its oxidation products have an influence on the resin surface and/or aqueous speciation of An(IV).

Fig. 1 shows a clear decrease of $R_d^0$ values of Np(IV) at increasing S : L ratio. Although this behaviour is not understood so far, previous observations made in sorption studies with Th(IV) on calcite indicate that aqueous speciation is not affected and therefore Np(IV)-GLU complexes can be properly studied using the Schubert method provided that the $R_d^0$ and $R_d$ values used for data analysis have been determined from experiments using the same S : L ratio [13].

### 3.2 Effect of GLU on Np(IV) sorption: determination of the stoichiometry and stability constants of Np(IV)-GLU complexes

Fig. 2 shows the $R_d$ values for the sorption of Np(IV) on the Bio-Rad resin and the tube walls at increasing [GLU], for both pH = 13.3 (Fig. 2a) and 11 (Fig. 2b). As previously discussed in Sect. 3.1, $R_d^0$ values for the experiments at S : L = $10^{-3}$ kg L$^{-1}$ and $10^{-2}$ kg L$^{-1}$ differ significantly (*ca.* 0.5 log-units). Applying the corresponding $R_d^0$ value, *i.e.* the value determined at the same S : L ratio as the one used for measuring $R_d$ values in the presence of GLU, this effect does not influence the $R_d$ dependence of the GLU concentration and consequently, it has no effect on the determination of the stoichiometry and formation constants of the Np(IV)–GLU complexes. This is further confirmed by sorption data on tube walls in the same experiments (see Fig. 2a).

For both pH = 13.3 and 11, the effect of GLU on Np(IV) sorption is negligible up to a concentration of $\sim 10^{-6}$ M. Eq. (7) was used to fit the experimental data, allowing the determination of the number of GLU ligands, $n$, involved in the complexation reaction: $n = 1.08 \pm 0.15$ at pH 13.3 and $n = 0.92 \pm 0.15$ at pH 11. These results indicate the formation of a 1 : 1 Np(IV) : GLU complex in the absence of Ca, in good agreement with previous studies carried out for the systems Th(IV)-, U(IV)-, and Pu(IV)-GLU [5, 7, 14–17]. In the subsequent step, the experimental data were re-fitted, fix-

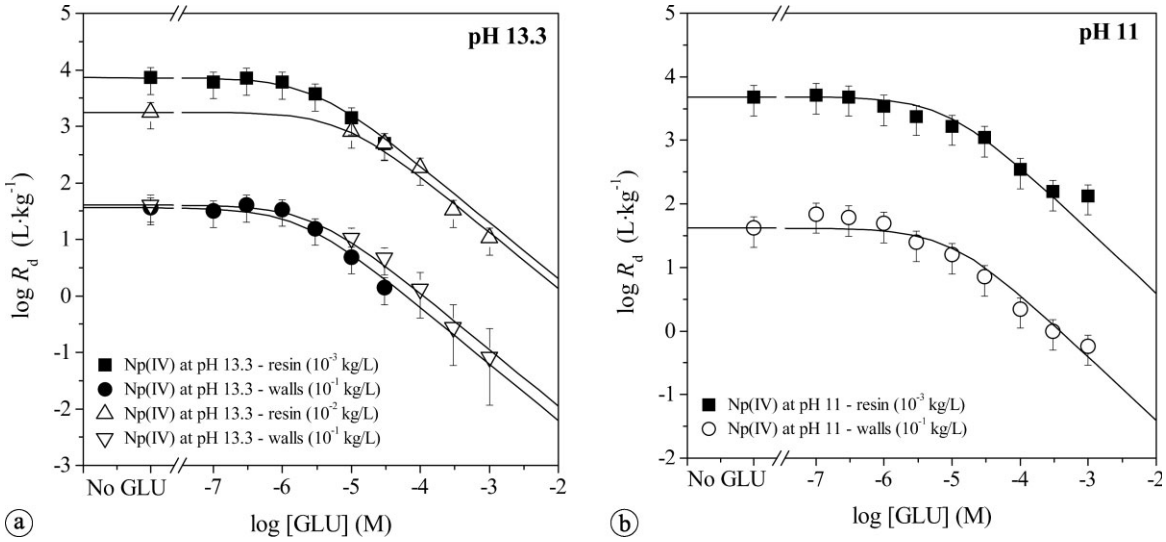


**Fig. 2.** Influence of GLU on Np(IV) sorption on Bio-Rad resin and on the tube walls at (**a**) pH = 13.3 (0.3 M NaOH, $I$ = 0.3 M) and (**b**) pH = 11.0 ($10^{-3}$ M NaOH, 0.3 M $NaClO_4$, $I$ = 0.3 M).

**Table 3.** Conditional stability constants (log ${}^{*}\beta'_{1,m,1}$ and log ${}^{*}\beta_{1,4,1}$) calculated for all experimental series, and resulting standard stability constant (log ${}^{*}\beta^{0}_{1,4,1}$) for the formation of the complex $Np(OH)_4GLU^-$ according with Eq. (3).

| pH | Sorbent | S : L (kg/L) | $I$ | $R_d^0$ ($L\,kg^{-1}$) | log ${}^{*}\beta'_{1,m,1}$ | log ${}^{*}\beta_{1,4,1}$ | log ${}^{*}\beta^{0}_{1,4,1}$ |
|---|---|---|---|---|---|---|---|
| 13.3 | Resin | $1\times10^{-3}$ | 0.3 M NaOH | $(7.3\pm3.7)\times10^{3}$ | $48.48\pm0.15$ | $-4.35\pm0.15$ | |
| 13.3 | Resin | $1\times10^{-2}$ | 0.3 M NaOH | $(1.8\pm0.9)\times10^{3}$ | $48.04\pm0.16$ | $-4.81\pm0.16$ | |
| 13.3 | Walls | 0.1 | 0.3 M NaOH | $(3.7\pm1.9)\times10^{1}$ | $48.68\pm0.15$ | $-4.14\pm0.15$ | |
| 13.3 | Walls | 0.1 | 0.3 M NaOH | $(4.1\pm2.0)\times10^{1}$ | $48.48\pm0.16$ | $-4.34\pm0.16$ | |
| 11 | Resin | $1\times10^{-3}$ | 0.3 M $NaClO_4$ | $(5.1\pm2.6)\times10^{3}$ | $39.18\pm0.15$ | $-4.75\pm0.15$ | |
| 11 | Walls | 0.1 | 0.3 M $NaClO_4$ | $(4.9\pm2.5)\times10^{1}$ | $39.11\pm0.15$ | $-4.81\pm0.15$ | |
| | | | $I=0$ | | | | $-2.92\pm0.30$ |

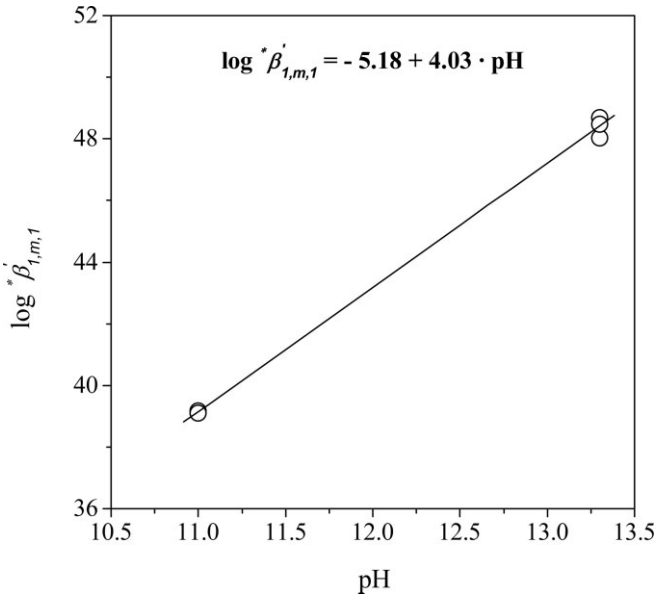


**Fig. 3.** Determination of the number of protons ($m$) involved in the complexation reaction between Np(IV) and GLU.

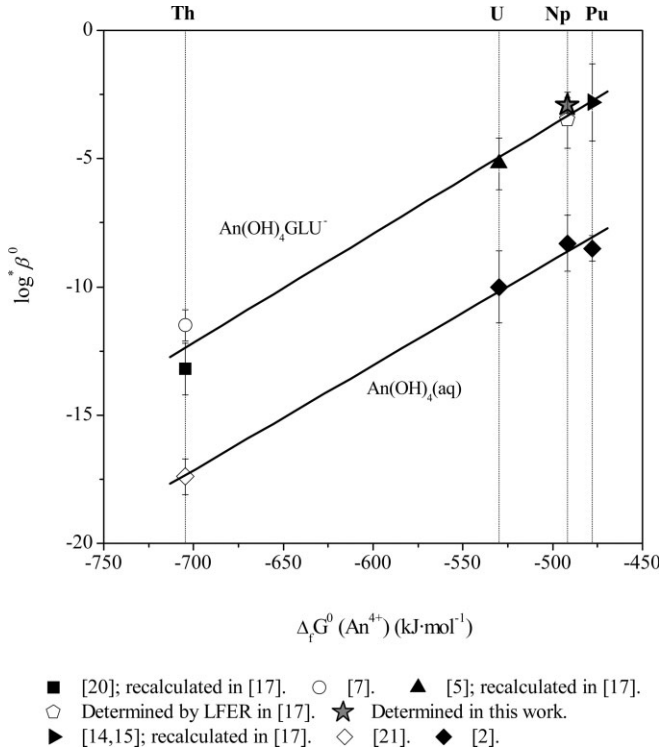


**Fig. 4.** LFER for An(IV)$(OH)_4GLU^-$ and An(IV)$(OH)_4$(aq) complexes (An(IV) = Th, U, Np, Pu). The grey asterisk corresponds to log ${}^{*}\beta^{0}_{1,4,1}$ determined in this work for $Np(OH)_4GLU^-$.

ing the value of "n" to 1 in order to determine the conditional formation constant of the Np – GLU complex in each experiment. The resulting values for log ${}^{*}\beta'_{1,m,1}$ are listed in Table 3.

Fig. 3 shows the correlation between log ${}^{*}\beta'_{1,m,1}$ and pH. The slope of this linear correlation provides the number of protons involved in the complexation reaction ($m$, see Sect. 2.4), which for Np(IV)-GLU is found to be 4. Consequently, conditional stability constants, log ${}^{*}\beta_{1,4,1}$ ($I$ = 0.3 M), were calculated on the assumption that four protons were involved and by considering the pH in each experimental series (Table 3). An unweighted average of log ${}^{*}\beta_{1,4,1}$ was determined and corrected to $I$ = 0 with the Davies equation, resulting in log ${}^{*}\beta^{0}_{1,4,1} = -2.92\pm0.30$.

### 3.3 Comparison with other actinides: linear free-energy relationships

Linear free-energy relationship (LFER) are often used to assess the reliability of stability constants along the An(IV) series [17–19]. The log ${}^{*}\beta^{0}_{1,4,1}$ value determined in this work was compared with other data available in the literature for An(IV)$(OH)_4GLU^-$ complexes. In addition, log ${}^{*}\beta^{0}_{1,4,1}$ as reported in the NEA reviews [2, 21] for the An(IV) series, were considered in the LFER for comparison purposes. Fig. 4 shows a very similar trend along the An(IV) series for both An$(OH)_4GLU^-$ and An$(OH)_4$(aq) complexes. Log ${}^{*}\beta^{0}_{1,4,1}$ determined for Np(IV) is very similar to the value re-calculated in [17] for Pu(IV), in agreement with the similarities in $\Delta_f G^0_m(An^{4+})$ and ionic radii of the two actinides.

## 4. Conclusions

The formation of a Np(IV)-GLU complex with stoichiometry $Np(OH)_4GLU^-$ has been demonstrated under hyperalkaline reducing conditions. The application of the Schubert method to a series of sorption experiments at different

pH and $[GLU]_{tot}$ permitted the determination of the complexation constant: $\log {}^{*}\beta^{0}_{1,4,1} = -2.92 \pm 0.30$. Both stoichiometry and stability are consistent with data available for Th(IV)-, U(IV)- and Pu(IV)-GLU complexes, as indicated by the linear free-energy relationships, LFER.

The newly identified complex is expected to dominate the Np(IV) speciation at $[GLU]_{free} > 10^{-6}$ M under alkaline conditions. In cement-based repositories, however, the impact on Np(IV) sorption and solubility is considered to be limited, due to the significantly lower $[GLU]_{free}$ expected ($\sim 10^{-7}$ M). This conclusion might be revisited if ternary Ca-Np(IV)-GLU complexes form, as previously described for Th(IV) [4, 6].

*Acknowledgment.* The research leading to these results has received funding from National Cooperative for the Disposal of Radioactive Waste (NAGRA), Switzerland. Henar Rojo acknowledges CIEMAT for funding a part of her stay at Paul Scherrer Institute.

## References

1. Schubert, J., Lindenbaum, A.: Stability of alkaline earth–organic acid complexes measured by ion exchange. J. Am. Chem. Soc. **74**, 3529 (1952).
2. Guillaumont, R., Fanghänel, Th., Fuger, J., Grenthe, I., Neck, V., Palmer, D., Rand, M.: Update on the chemical thermodynamics of uranium, neptunium, plutonium, americium and technetium. In: *Chemical Thermodynamics*. Vol. 5 (Mompean, F. J. *et al.*, eds.) Elsevier, North-Holland, Amsterdam (2003).
3. Wieland, E. and van Loon, L. R.: Cementitious near-field sorption database for performance assessment of an ILW repository in opalinus clay. PSI-Bericht 03-06, Paul Scherrer Institut, Villigen, Switzerland and Nagra Technical Report NTB 02-20, Wettingen, Switzerland (2003).
4. Vercammen, K., Glaus, M. A., Van Loon, L. R.: Complexation of Th(IV) and Eu(III) by $\alpha$-isosaccharinic acid under alkaline conditions. Radiochim. Acta **89**, 393 (2001).
5. Warwick, P., Evans, N., Hall, T., Vines, S.: Stability constants of uranium (IV)-$\alpha$-isosaccharinic acid and gluconic acid complexes. Radiochim. Acta **92**, 897 (2004).
6. Tits, J., Wieland, E., Bradbury, M. H.: The effect of isosaccharinic acid and gluconic acid on the retention of Eu(III), Am(III) and Th(IV) by calcite. Appl. Geochem. **20**, 2082 (2005).
7. Colàs, E., Grivé, M., Rojo, I., Duro, L.: Solubility of $ThO_2 \cdot xH_2O$(am) in the presence of gluconate. Radiochim. Acta **99**, 269 (2011).
8. Warwick, P., Evans, N., Hall, T., Vines, S.: Complexation of Ni(II) by $\alpha$-isosaccharinic acid and gluconic acid from pH 7 to pH 13. Radiochim. Acta **91**, 233 (2003).
9. Sill, C. W.: Preparation of neptunium-239 tracer. Anal. Chem. **38**, 802 (1966).
10. Rai, D., Hess, N. J., Xia, Y., Rao, L., Cho, H. M., Moore, R. C., Van Loon, L. R.: Comprehensive thermodynamic model applicable to highly acidic to basic conditions for isosaccharinate reactions with Ca(II) and Np(IV). J. Solution Chem. **32**, 665 (2003).
11. Puigdomènech, I.: INPUT, SED and PREDOM: Fortran Programs Drawing Equilibrium Diagrams. Technical report TRITA-OOK-3010, Royal Institute of Technology, Stockholm, Sweden (1983).
12. Grenthe, I., Wanner, H.: Guidelines for the extrapolation to zero ionic strength. OECD-NEA, Issy-les-Moulineaux (France) (2000).
13. Tits, J., Wieland, E., Bradbury, M. H., Eckert, P., Schaible, A.: The uptake of Eu(III) and Th(IV) by calcite under high pH cement pore water conditions. PSI Report 02-03, Paul Scherrer Institut, Villigen, Switzerland and Nagra Technical Report NTB 02-08, Nagra, Wettingen, Switzerland (2002).
14. Cross, J. E., Ewart, F. T., Greenfield, B. F.: Modelling the behaviour of organic degradation products. Mater. Res. Soc. Symp. Proc. **127**, 715 (1989).
15. Moreton, A. D.: Thermodynamic modelling of the effect of hydroxycarboxylic acids on the solubility of plutonium at high pH. Mater. Res. Soc. Symp. Proc. **294**, 753 (1993).
16. Greenfield, B. F., Holtom, G. J., Hurdus, M. H., O'Kelly, N., Pilkington, N. J., Rosevear, A., Spindler, M. W., Williams, S. J.: The identification and degradation of isosaccharinic acid, a cellulose degradation product. Mater. Res. Soc. Symp. Proc. **353**, 1151 (1995).
17. Gaona, X., Montoya, V., Colàs, E., Grivé, M., Duro, L.: Review of the complexation of tetravalent actinides by ISA and gluconate under alkaline to hyperalkaline conditions. J. Contam. Hydrol. **102**, 217 (2008).
18. Choppin, G. R., Thakur, P., Mathur, J. N.: Complexation thermodynamics and structural aspects of actinide-aminopolycarboxylates. Coord. Chem. Rev. **250**, 936 (2006).
19. Meyer, M., Burgat, R., Faure, S., Batifol, B., Hubinois, J. C., Chollet, H., Guilard, R.: Thermodynamic studies of actinide complexes. 1. A reappraisal of the solution equilibria between plutonium(IV) and ethylendiaminetetraacetic acid ($EDTAH_4$) in nitric media. Compt. Rend. Chim. **10**, 929 (2007).
20. Felmy, A. R.: Chemical speciation of americium, curium and selected tetravalent actinides in high level waste. Technical Report, PNNL. EMSP Project 73749 (2004).
21. Rand, M. H., Fuger, J., Grenthe, I., Neck, V., Rai, D.: Chemical thermodynamics of thorium. In: *Chemical Thermodynamics*. Vol. 11, OECD Nuclear Energy, Paris (2008).